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(54) **A non-hydrous electrolyte lithium primary cell and a method for manufacturing manganese dioxide therefor.**

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## Description

The present invention relates to a non-hydrous electrolyte lithium primary cell comprising lithium or a lithium alloy as an anode active material and manganese dioxide as a cathode active material and to a method for manufacturing manganese dioxide for the lithium primary cell.

Manganese dioxide and carbon fluoride are known as typical examples of a cathode active material of a lithium primary cell and are already commercially available.

Of these cathode active materials, manganese dioxide is advantageous since it has good storage stability and is inexpensive.

A lithium primary cell using manganese dioxide as a cathode active material is currently applied to a camera and the like. As the multi-function operations of a camera has progressed, a demand has arisen for a lithium primary cell to have a high discharge voltage. A large discharge capacity, i.e. a long discharge time is also demanded for the lithium primary cell. No lithium primary cell, however, which can satisfy both the requirements with a good balance, has been proposed.

The present invention has been made in consideration of the above situation and is intended to provide a lithium primary cell which uses manganese dioxide as a cathode active material and achieves both a high discharge voltage and a long discharge time and a method for manufacturing manganese dioxide for the lithium primary cell.

According to the present invention, manganese dioxide containing phosphorus is used as the cathode active material. When this cathode active material is used for manufacturing a lithium primary cell, both a high discharge voltage and a long discharge time are achieved.

According to the present invention there is provided a non-hydrous electrolyte lithium primary cell comprising lithium or a lithium alloy as an anode active material and a cathode active material which consists of manganese dioxide containing 0.05 to 2.0 parts by weight of phosphorus per 100 parts by weight of manganese dioxide and having a specific surface area of 49 to 150 m<sup>2</sup>/g, said manganese dioxide being prepared by introducing a manganese sulfate solution and sulfuric acid as an electrolyte into an electrolytic cell, adding to said electrolyte at least one member selected from phosphoric acid, phosphorous acid, hypophosphorous acid and compounds thereof and carrying out the electrolysis at a bath temperature of 94 to 100 °C whereby manganese dioxide containing phosphorus is electrodeposited on the cathode.

Further in accordance with the present invention there is provided a method of manufacturing manganese dioxide for a non-hydrous electrolyte lithium primary cell containing 0.05 to 2.0 parts by weight of phosphorus per 100 parts by weight of manganese dioxide and having a specific surface area of 49 to 150 m<sup>2</sup>/g which consists of introducing a manganese sulfate solution and sulfuric acid as an electrolyte into an electrolytic cell, adding to said electrolyte at least one member selected from phosphoric acid, phosphorous acid, hypophosphorous acid and compounds thereof and carrying out the electrolysis at a bath temperature of 94 to 100 °C whereby manganese dioxide containing phosphorus is electrodeposited on the cathode.

If the phosphorus content is less than 0.05 parts by weight with respect to 100 parts by weight of manganese dioxide, no sufficient addition effect is obtained in terms of discharge characteristics of a manufactured lithium primary cell. If the phosphorus content exceeds 2.0 parts by weight, discharge characteristics of manganese dioxide of a manufactured lithium primary cell are degraded.

In this manufacturing method, manganese sulfate and a sulfuric acid solution are used as an electrolyte. Generally, in this electrolyte, the manganese concentration is 20 to 50 g/l, and the sulfuric acid concentration is 30 to 89 g/l. In addition, as electrodes, titanium or the like may be used as the cathode, and carbon or the like may be used as the anode.

Electrolytic conditions for electrolytic manganese dioxide are generally a bath temperature of 94 to 100 °C and a current density of 50 to 100 A/m<sup>2</sup>.

In this manufacturing method, phosphoric acid, phosphorous acid, hypophosphorous acid, or compounds thereof are added to the electrolyte. Examples of such compounds are sodium salts, potassium salts and the like of phosphoric acid, phosphorous acid, and hypophosphorous acid. The phosphoric acid compounds or the like are uniformly added together with a manganese sulfate supply solution from an upper portion of an electrolytic cell to between electrode plates.

The concentration of the phosphoric acid compound or the like in the electrolyte is set to be 0.1 to 3.0 g/l, and the electrolytic conditions are adjusted so that phosphorus is contained in an amount falling within the above range in the manufactured electrolytic manganese dioxide.

The electrolytic manganese dioxide manufactured as described above has a large specific surface area of 49 to 150 m<sup>2</sup>/g. If the specific surface area of electrolytic manganese dioxide is smaller than the above value, reaction area with respect to an electrolyte is small and load discharge performance is weak when

this electrolytic manganese dioxide is used as a cathode active material to manufacture a lithium primary cell. If the specific surface area of electrolytic manganese dioxide exceeds the above value, a cathode agent becomes bulky. The specific surface area of electrolytic manganese dioxide can be adjusted by arbitrarily selecting the type or content of the phosphoric acid compound.

5 A lithium primary cell, manufactured under normal conditions by using electrolytic manganese dioxide containing phosphorus as a cathode active material and lithium or a lithium alloy such as lithium-aluminum as an anode, has a higher discharge voltage and a longer discharge time than those of a conventional lithium primary cell.

#### 10 BRIEF DESCRIPTION OF THE DRAWINGS:

Fig. 1 is a schematic sectional view for explaining a test cell used in examples and a comparative example; and

15 Figs. 2 and 3 are graphs each showing a relationship between a voltage and a continuous discharge time in the examples and comparative example.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT:

The present invention will be described in detail below by way of its examples.

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##### Example 1

A titanium plate as a cathode and a graphite plate as an anode were alternately suspended in an electrolytic cell having a volume of 3 l and equipped with a heating apparatus, and an addition tube was connect to the bottom portion of the electrolytic cell to add an electrolytic supply solution composed of manganese sulfate and a phosphoric acid solution.

The electrolytic supply solution was adjusted so that 0.5 g/l of phosphoric acid were contained in the manganese sulfate solution.

30 When electrolysis was performed by supplying the supply solution in the electrolytic cell, the composition of the electrolyte was adjusted so that 50 g/l of manganese and 30 g/l of sulfuric acid were contained. Electrolysis was performed at a bath temperature of  $95 \pm 1^\circ\text{C}$  and a current density of 100 A/m<sup>2</sup>.

After electrolysis was finished, the cathode plate on which electrolytic manganese dioxide was electro-deposited was removed from the cell and subjected to a normal post-treatment, and the specific surface area of the obtained electrolytic manganese dioxide was measured. The measurement results are listed in Table 1.

35 A heat treatment was performed at 400°C for three hours, 0.135 g of the obtained electrolytic manganese dioxide were measured, and 0.09 g of graphite and 0.06 g of an tetrafluoroethylene resin were mixed therewith. The resultant mixture was pressure-molded at 3 t/cm<sup>2</sup> to prepare a cathode mixture. Note that the manganese dioxide, the graphite and the tetrafluoroethylene were predried and mixed.

40 The prepared cathode mixture was used to form a test cell as shown in Fig. 1, and a 2.5-K $\Omega$  continuous discharge test was performed at 20°C. All these operations were performed in a dry box in an argon atmosphere. The electrolyte was prepared by dissolving 1 mol/l of lithium perchlorate in a 1 : 1 solvent mixture of propylenecarbonate and 1,2-dimethoxyethane. A reagent used in this test was dried by a conventional method. In addition, the anode was formed by punching a metal lithium sheet to have the same diameter as that of the cathode mixture.

45 In the test cell shown in Fig. 1, reference numeral 1 denotes an anode terminal for externally extracting a current; and 2, insulating members made of a teflon® resin. The insulating members 2 are threadably engaged with each other to close the cell. Reference numeral 3 denotes an anode plate; 4, a crimped metal lithium sheet (anode); 5, a separator made of a non-woven fabric; 6, a cathode mixture formed by the above method; and 7, a stainless steel cathode.

50 A discharge test was performed by using the above test cell. The obtained relationship between a voltage and a continuous discharge time is shown in Fig. 2.

##### Examples 2 and 3

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By using an apparatus similar to that used in Example 1, electrolysis was performed by changing a phosphorus addition amount as listed in Table 1, and a post-treatment was performed following the same procedures as in Example 1. The specific surfaces area of the obtained electrolytic manganese dioxides are

listed in Table 1.

A heat treatment was performed following the same procedures as in Example 1, and a test cell as shown in Fig. 1 was manufactured following the same procedures as in Example 1 by using each electrolytic manganese dioxide. A discharge test was performed by using this test cell. The obtained relationship between a voltage and a continuous discharge time is shown in Fig. 2.

#### Examples 4 - 7

By using an apparatus similar to that used in Example 1, electrolysis was performed by adding phosphorous acid, hypophosphorous acid, sodium tripolyphosphate, and potassium tripolyphosphate in amounts as listed in Table 1, instead of phosphoric acid, and a post treatment was performed following the same procedures as in Example 1. The specific surfaces area of the obtained electrolytic manganese dioxides are listed in Table 1.

A heat treatment was performed following the same procedures as in Example 1, and a test cell was manufactured following the same procedures as in Example 1 by using each electrolytic manganese dioxide. A discharge test was performed by using this test cell. The obtained relationship between a voltage and a continuous discharge time is listed in Fig. 3.

#### Comparative Example 1

By using an apparatus similar to that used in Example 1, electrolysis was performed following the same procedures as in Example 1 except that no phosphoric acid solution was added, and a post-treatment was performed following the same procedures as in Example 1. The specific surface area of the obtained electrolytic manganese dioxide is listed in Table 1.

A heat treatment was performed following the same procedures as in Example 1, and a test cell as shown in Fig. 1 was manufactured following the same procedures as in Example 1 by using this electrolytic manganese dioxide. A discharge test was performed by using this test cell. The obtained relationship between a voltage and a continuous discharge time is shown in Figs. 2 and 3 so as to be compared with the examples.

Table 1

Example. Comparative Example	Electrolytic Conditions					Electrolytic Voltage (V)	Specific Surface area (m <sup>2</sup> /g)	Phosphorus Content of Electrolytic Manganese Dioxide *1
	Current Density (A/m <sup>2</sup> )	Electrolyte Composition		Additive	Addition Amount (g/l)			
		Mn (g/l)	H <sub>2</sub> SO <sub>4</sub> (g/l)					
Example 1	100	50	30	H <sub>3</sub> PO <sub>4</sub>	0.5	2.1 to 2.5	49	0.05
Example 2	100	50	30	H <sub>3</sub> PO <sub>4</sub>	1.0	2.1 to 2.3	63	0.52
Example 3	100	50	30	H <sub>3</sub> PO <sub>4</sub>	3.0	2.0 to 3.0	150	2.00
Example 4	100	50	30	H <sub>3</sub> PO <sub>3</sub>	0.5	1.8 to 2.1	56	0.63
Example 5	100	50	30	Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	1.0	1.6 to 2.0	60	1.53
Example 6	100	50	30	K <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	0.5	1.9 to 2.5	52	0.98
Example 7	100	50	30	H <sub>3</sub> PO <sub>2</sub>	0.5	1.8 to 2.1	60	0.68
Comparative Example 1	100	50	30	-	-	1.9 to 2.3	38	0.0006

\*1 : amount (parts by weight) with respect to 100 parts by weight of manganese dioxide

As is apparent from Figs. 2 and 3, the test cell obtained by each of Examples 1 to 7 had a much longer continuous discharge time and a higher operation voltage during discharge than those of the test cell obtained by Comparative Example 1. That is, each test cell according to the present invention had very good cell characteristics as a non-hydrous electrolyte cell.

As has been described above, according to the method of the present invention, a phosphoric acid compound or the like is added in an electrolyte upon manufacturing of electrolyte manganese dioxide by electrolysis using manganese sulfate and a sulfuric acid solution as the electrolyte. Therefore, the obtained electrolyte manganese dioxide has a larger specific surface area than that of conventional electrolytic manganese dioxide and contains a predetermined amount of phosphorus.

In addition, by using this electrolytic manganese dioxide containing phosphorus as a cathode active material of a lithium primary material, a high discharge voltage and a long discharge time can be achieved.

Since the high discharge voltage and long discharge time can be simultaneously achieved, cell characteristics of the lithium primary cell can be effectively improved.

## Claims

1. A non-hydrous electrolyte lithium primary cell comprising lithium or a lithium alloy as an anode active material and a cathode active material which consists of manganese dioxide containing 0.05 to 2.0 parts by weight of phosphorus per 100 parts by weight of manganese dioxide and having a specific surface area of 49 to 150m<sup>2</sup>/g, said manganese dioxide being prepared by introducing a manganese sulfate solution and sulfuric acid as an electrolyte into an electrolytic cell, adding to said electrolyte at least one member selected from phosphoric acid, phosphorous acid, hypophosphorous acid and compounds thereof and carrying out the electrolysis at a bath temperature of 94 to 100 °C whereby manganese dioxide containing phosphorus is electrodeposited on the cathode.
2. A method of manufacturing manganese dioxide for a non-hydrous electrolyte lithium primary cell containing 0.05 to 2.0 parts by weight of phosphorus per 100 parts by weight of manganese dioxide and having a specific surface area of 49 to 150m<sup>2</sup>/g, which consists in introducing a manganese sulfate solution and sulfuric acid as an electrolyte into an electrolytic cell, adding to said electrolyte at least one member selected from phosphoric acid, phosphorous acid, hypophosphorous acid and compounds thereof and carrying out the electrolysis at a bath temperature of 94 to 100 °C whereby manganese dioxide containing phosphorus is electrodeposited on the cathode.
3. A lithium primary cell as claimed in claim 1, in which said electrolysis is carried out at a current density of 50 to 100 A/m<sup>2</sup>.
4. A method as claimed in claim 2, in which said electrolysis is carried out at a current density of 50 to 100 A/m<sup>2</sup>.
5. A lithium primary cell as claimed in claim 1 or 3, in which the manganese concentration of said electrolyte is 20 to 50 g/l.
6. A method as claimed in claim 2 or 4, in which the manganese concentration of said electrolyte is 20 to 50 g/l.
7. A lithium primary cell as claimed in claim 1, 3 or 5, in which the sulfuric acid concentration of said electrolyte is 30 to 80 g/l.
8. A method as claimed in claim 2, 4 or 6, in which the sulfuric acid concentration of said electrolyte is 30 to 80 g/l.
9. A lithium primary cell as claimed in claim 1, 3, 5, or 7, in which said cathode during the electrolytic deposition of manganese dioxide is a titanium plate.
10. A method as claimed in claim 2, 4, 6, or 8, in which said cathode during the electrolytic deposition of manganese dioxide is a titanium plate.
11. A lithium primary cell as claimed in claim 1, 3, 5, 7 or 9, in which said member is added to said electrolyte in a concentration of 0.1 to 3.0 g/l.
12. A method as claimed in claim 2, 4, 6, 8, or 10, in which said member is added to said electrolyte in a concentration of 0.1 to 3.0 g/l.

## Patentansprüche

1. Lithium-Primärzelle mit einem nicht-wäßrigen Elektrolyten, dadurch **gekennzeichnet**, daß sie Lithium oder eine Lithiumlegierung als anodenaktives Material und ein kathodenaktives Material enthält, das aus Mangandioxid besteht, das 0,05 bis 2,0 Gewichtsteile Phosphor pro 100 Gewichtsteile Mangandioxid enthält und das eine spezifische Oberfläche von 49 bis 150 m<sup>2</sup>/g aufweist, wobei das Mangandioxid durch Einbringen einer Mangansulfatlösung und Schwefelsäure als Elektrolyt in eine elektrolytische Zelle, Versetzen des Elektrolyten mit mindestens einer Verbindung, ausgewählt aus Phosphorsäure, Phosphoriger Säure, Hypophosphoriger Säure und Verbindungen davon und Durchführen der Elektrolyse bei einer Badtemperatur von 94 bis 100 °C, wodurch das phosphorenhaltende Mangandioxid auf der Kathode galvanisch abgeschieden wird, hergestellt worden ist.
2. Verfahren zur Herstellung von Mangandioxid für eine Lithium-Primärzelle mit einem nicht-wäßrigen Elektrolyten, das 0,05 bis 2,0 Gewichtsteile Phosphor pro 100 Gewichtsteile Mangandioxid enthält und eine spezifische Oberfläche von 49 bis 150 m<sup>2</sup>/g aufweist, dadurch **gekennzeichnet**, daß man eine Mangansulfatlösung und Schwefelsäure als Elektrolyt in eine elektrolytische Zelle einbringt, den Elektrolyten mit mindestens einer Verbindung, ausgewählt aus Phosphorsäure, Phosphoriger Säure, Hypophosphoriger Säure und Verbindungen davon, versetzt und die Elektrolyse bei einer Badtemperatur von 94 bis 100 °C durchführt, wodurch phosphorenhaltendes Mangandioxid auf der Kathode galvanisch abgeschieden wird.
3. Lithium-Primärzelle nach Anspruch 1, dadurch **gekennzeichnet**, daß die Elektrolyse bei einer Stromdichte von 50 bis 100 A/m<sup>2</sup> durchgeführt worden ist.
4. Verfahren nach Anspruch 2, dadurch **gekennzeichnet**, daß man die Elektrolyse bei einer Stromdichte von 50 bis 100 A/m<sup>2</sup> durchführt.
5. Lithium-Primärzelle nach Anspruch 1 oder 3, dadurch **gekennzeichnet**, daß die Mangankonzentration des Elektrolyten 20 bis 50 g/l beträgt.
6. Verfahren nach Anspruch 2 oder 4, dadurch **gekennzeichnet**, daß die Mangankonzentration des Elektrolyten 20 bis 50 g/l beträgt.
7. Lithium-Primärzelle nach Anspruch 1, 3 oder 5, dadurch **gekennzeichnet**, daß die Schwefelsäurekonzentration des Elektrolyten 30 bis 80 g/l beträgt.
8. Verfahren nach Anspruch 2, 4 oder 6, dadurch **gekennzeichnet**, daß die Schwefelsäurekonzentration des Elektrolyten 30 bis 80 g/l beträgt.
9. Lithium-Primärzelle nach Anspruch 1, 3, 5 oder 7, dadurch **gekennzeichnet**, daß die Kathode während der elektrolytischen Abscheidung des Mangandioxids eine Titanplatte ist.
10. Verfahren nach Anspruch 2, 4, 6 oder 8, dadurch **gekennzeichnet**, daß die Kathode während der elektrolytischen Abscheidung des Mangandioxids eine Titanplatte ist.
11. Lithium-Primärzelle nach Anspruch 1, 3, 5, 7 oder 9, dadurch **gekennzeichnet**, daß die Verbindung dem Elektrolyten in einer Konzentration von 0,1 bis 3,0 g/l zugesetzt worden ist.
12. Verfahren nach Anspruch 2, 4, 6, 8 oder 10, dadurch **gekennzeichnet**, daß man die Verbindung dem Elektrolyten in einer Konzentration von 0,1 bis 3,0 g/l zusetzt.

## Revendications

1. Pile au lithium à électrolyte anhydre comprenant du lithium, ou un alliage de lithium, comme matière active d'anode et une matière active de cathode qui est constituée de dioxyde de manganèse contenant de 0,05 à 2,0 parties, en poids, de phosphore pour 100 parties, en poids, de dioxyde de manganèse et ayant une surface spécifique de 49 à 150 m<sup>2</sup>/g, ledit dioxyde de manganèse étant préparé en introduisant une solution de sulfate de manganèse et d'acide sulfurique comme électrolyte



dans une cellule d'électrolyse, en ajoutant audit électrolyte au moins un élément choisi parmi l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux et leurs composés, et en réalisant l'électrolyse à une température de bain de 94 à 100° C, ce par quoi le dioxyde de manganèse contenant du phosphore est déposé par électrolyse sur la cathode.

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2. Procédé de fabrication de dioxyde de manganèse pour une pile au lithium à électrolyte anhydre contenant de 0,05 à 2,0 parties, en poids, de phosphore pour 100 parties, en poids, de dioxyde de manganèse et ayant une surface spécifique de 49 à 150 m<sup>2</sup>/g, qui comprend l'introduction d'une solution de sulfate de manganèse et d'acide sulfurique comme électrolyte dans une cellule d'électrolyse, l'ajout audit électrolyte d'au moins un élément choisi parmi l'acide phosphorique, l'acide phosphoreux, l'acide hypophosphoreux et leurs composés, et l'exécution de l'électrolyse à une température de bain de 94 à 100° C, ce par quoi le dioxyde de manganèse contenant du phosphore est déposé par électrolyse sur la cathode.

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3. Pile au lithium selon la revendication 1, dans laquelle ladite électrolyse est effectuée à une densité de courant de 50 à 100 A/m<sup>2</sup>.

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4. Procédé selon la revendication 2, dans lequel ladite électrolyse est effectuée à une densité de courant de 50 à 100 A/m<sup>2</sup>.

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5. Pile au lithium selon la revendication 1 ou 3, dans laquelle la concentration en manganèse dudit électrolyte est de 20 à 50 g/l.

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6. Procédé selon la revendication 2 ou 4, dans lequel la concentration en manganèse dudit électrolyte est de 20 à 50 g/l.

7. Pile au lithium selon la revendication 1, 3 ou 5, dans laquelle la concentration en acide sulfurique dudit électrolyte est de 30 à 80 g/l.

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8. Procédé selon la revendication 2, 4 ou 6, dans laquelle la concentration en acide sulfurique dudit électrolyte est de 30 à 80 g/l.

9. Pile au lithium selon les revendications 1, 3, 5 ou 7, dans laquelle ladite cathode, lors du dépôt électrolytique de dioxyde de manganèse, est une plaque de titane.

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10. Procédé selon les revendications 2, 4, 6 ou 8, dans lequel ladite cathode, lors du dépôt électrolytique de dioxyde de manganèse, est une plaque de titane.

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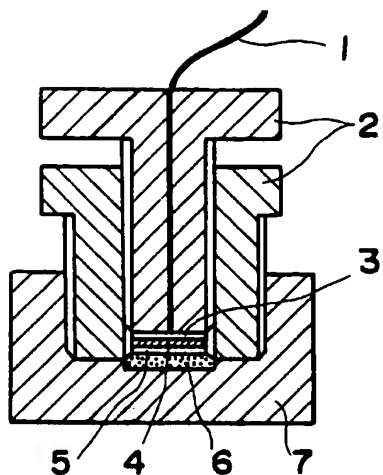
11. Pile au lithium selon les revendications 1, 3, 5, 7 ou 9, dans laquelle ledit élément est ajouté audit électrolyte en une concentration de 0,1 à 3,0 g/l.

12. Procédé selon les revendications 2, 4, 6, 8 ou 10, dans lequel ledit élément est ajouté audit électrolyte en une concentration de 0,1 à 3,0 g/l.

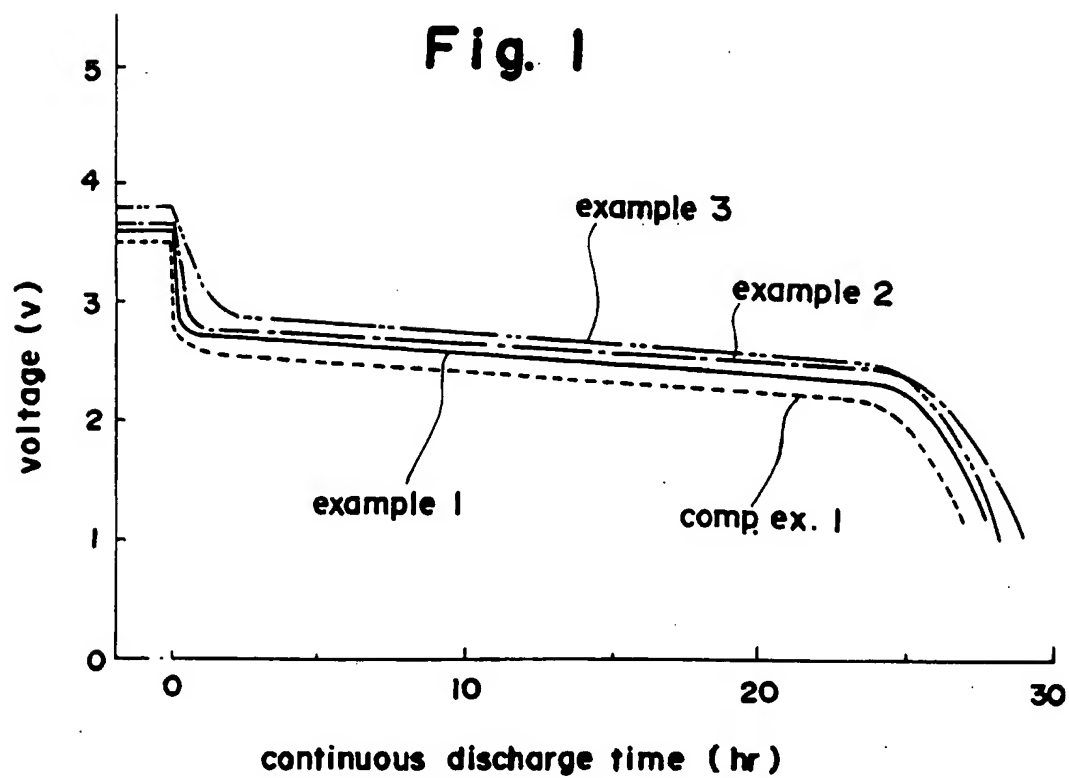
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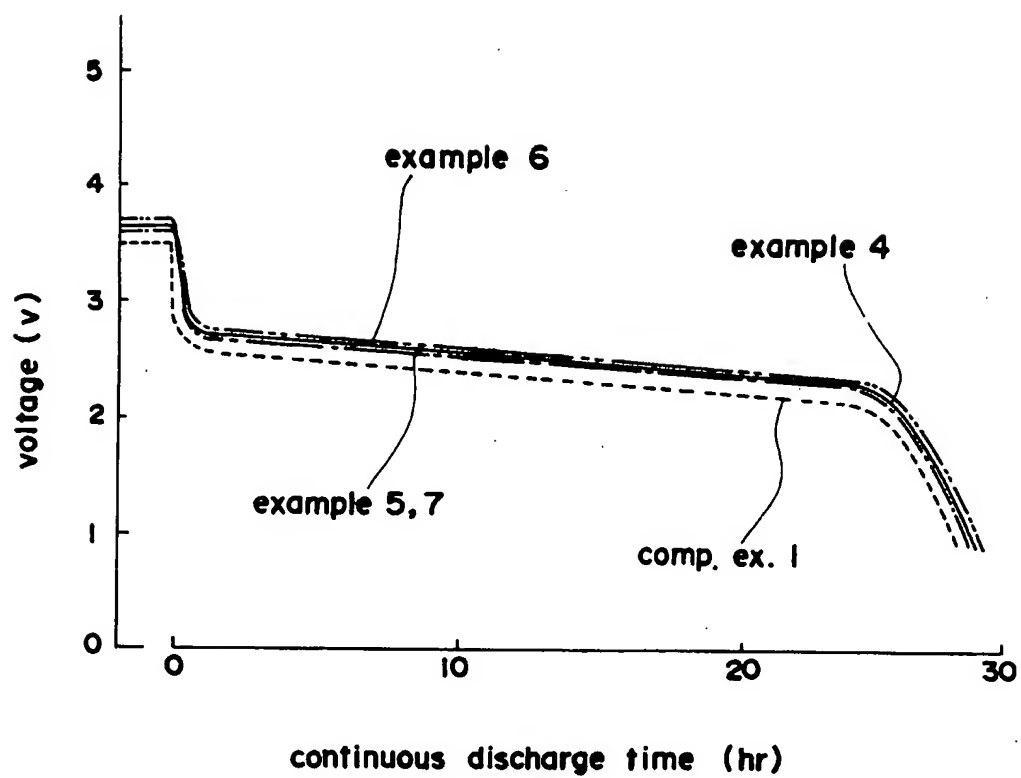
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**Fig. 1**



**Fig. 2**



**Fig. 3**